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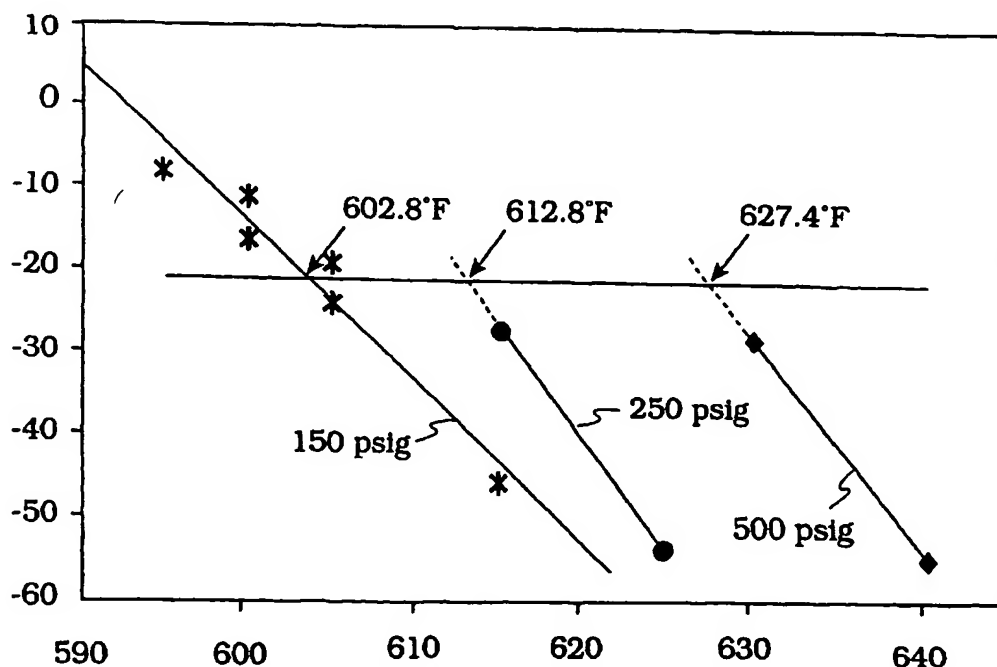
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(54) Title: ENHANCED LUBE OIL YIELD BY LOW HYDROGEN PRESSURE CATALYTIC DEWAXING OF PARAFFIN WAX



(57) Abstract: Catalytic dewaxing of paraffin containing feeds, preferably feeds produced from syn gas using a non-shifting Fischer-Tropsch catalyst, is accomplished at relatively low hydrogen partial pressures without substantial effect on the life of the dewaxing catalyst having a certain pore structure.



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ENHANCED LUBE OIL YIELD BY LOW HYDROGEN PRESSURE CATALYTIC DEWAXING OF PARAFFIN WAX

FIELD OF THE INVENTION

[0001] This invention relates to a process for catalytically dewaxing paraffin containing hydrocarbons. More particularly, this invention relates to the production of lube base oils having a pre-determined or pre-selected pour point by catalytically dewaxing a paraffin containing feed at low hydrogen partial pressures.

BACKGROUND OF THE INVENTION

[0002] The production of lube base oils by hydroprocessing paraffin containing feeds is well known, e.g., hydroisomerization or hydrocracking of the feed to produce lube base oils. These processes are catalytic and are usually carried out at relatively high hydrogen pressures, e.g., > 3549 kPa (500 psig) hydrogen partial pressures. Catalytic dewaxing is a form of hydroprocessing and involves paraffin isomerization and some hydrocracking in the production of lube base oils.

[0003] Hydrogen has always been used in the hydroprocessing, i.e., isomerization, cracking, dewaxing, of paraffins to produce lube base oils. Hydrogen is believed to be important for promoting extended catalyst life by e.g., reductive coke removal; see, for example U.S. Patent 4,872,968. Catalytic dewaxing is, essentially, the conversion of n-paraffins to branched paraffins. That is, the conversion of waxy molecules to molecules exhibiting better flow properties, particularly at lower temperatures. The hydrogen partial pressures usually employed in catalytic dewaxing processes range from about 1480 kPa (200 psig) to about 6996 kPa (1000 psig) or more, e.g., see U.S. Patent

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5,614,079 with hydrogen pressures in the higher end of this range being preferred - for reasons of catalyst life.

[0004] U.S. Patent 5,362,378 discloses hydrogen partial pressures of 597-1599 kPa (72-2305 psig) for use with large pore zeolite beta. This patent does not mention catalyst life or TIR, i.e., temperature increase required, necessary for maintaining product specifications, such as pour point or cloud point. Large pore zeolite beta is typically not classified as a dewaxing catalyst, but as an isomerization catalyst, and products produced utilizing such catalysts in accordance with U.S. Patent 5,362,378 would need to be dewaxed in order to achieve the low pour and cloud points obtained from the instant process.

[0005] We have now surprisingly found that a particular combination of features allows for conducting catalytic dewaxing at low hydrogen pressures of less than 3549 kPa (500 psig) and conditions that are selective to hydroisomerization, with little or no hydrocracking, good lube yield, and without sacrificing catalyst life, the product having low pour and cloud points.

SUMMARY OF THE INVENTION

[0006] According to the present invention, a feed containing at least 80 wt% n-paraffins is catalytically dewaxed in the presence of a catalyst comprising a molecular sieve with a one dimensional pore structure having an average diameter of 0.50 nm to 0.65 nm, and a metal dehydrogenation component, at hydrogen partial pressures of less than 3549 kPa (500 psig). The difference between the maximum diameter and the minimum diameter of the pores is preferably ≤ 0.05 nm. By using these process conditions, the catalyst deactivation rate as defined hereafter is maintained at a low level of less than 16.7 K (30°F)/year.

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[0007] The molecular sieve is, for example, ZSM-23, ZSM-35, ZSM-48, ZSM-22, SSZ-32, zeolite beta, mordenite and rare earth ion exchanged ferrierite.

[0008] The dehydrogenation component is usually a metal component, preferably manganese, tungsten, vanadium, zinc, chromium, molybdenum, rhenium, Group VIII metals such as nickel, cobalt, or noble metals such as platinum and palladium.

[0009] Catalyst deactivation rate is reported herein as TIR; that is "temperature increase required" for maintaining a pre-determined pour point (of preferably less than -12°C) or cloud point. The catalyst deactivation rate is determined by the difference in the initial temperature and the temperature at the end of a specified period of time, sufficient to maintain the pour point or cloud point target.

DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 is a plot of pour point, °C (ordinate) against temperature, °C (°F) (abscissa) showing that catalytic activity increases with decreasing hydrogen pressure.

[0011] Figure 2 is a plot of % conversion (ordinate) against pour point, °C (abscissa) showing that selectivity to isomerization increases with decreasing hydrogen pressure.

[0012] Figure 3 is a plot of average reactor temperature, °C (°F) (ordinate) against days on stream (abscissa) and shows a deactivation rate by regression

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when producing a lube base oil of -21°C pour point at a hydrogen partial pressure of 1135.5 kPa (150 psig).

[0013] Figure 4 is a plot of temperature, °C (ordinate) against days on stream (abscissa) at 1825 kPa (250 psig) hydrogen pressure to meet a diesel cloud point of -15°C.

[0014] Figure 5 is a plot similar to Figure 4 to meet a -21°C wide cut lube base oil pour point.

[0015] Figure 6 is a plot of reactor temperature, °C (°F) (ordinate) against days on stream (abscissa) to meet a -21°C pour point for a 371-510°C (700-950°F) isomerate.

[0016] Figure 7 is a plot of reactor temperature, °C (°F) (ordinate) against days on stream (abscissa) to meet a +8°C cloud point for a 510°C+ (950°F+) isomerate.

[0017] For the particular set of features described herein, reducing hydrogen partial pressure results in increased catalyst activity, and increased isomerization yield. That is, the increase in activity is almost entirely an increase in isomerization activity, and little hydrocracking occurs. Nevertheless, while decreasing hydrogen partial pressure would normally result in decreased catalyst life, the features of this invention show that catalyst life is not sacrificed.

[0018] For purposes of this invention, the pour point is determined by ASTM D-5950, the cloud point is determined by ASTM D-5773 and the pore parameters of the molecular sieve are determined by X-ray diffraction.

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DETAILED DESCRIPTION OF THE INVENTION

[0019] The feed that is employed in this invention is a paraffin containing feed that contains at least 80 wt% n-paraffins, more preferably greater than 90 wt% n-paraffins, still more preferably greater than 95 wt% n-paraffins and still more preferably 98 wt% n-paraffins. The feed generally boils in the range 221°C+ (430°F+), preferably 232°C+ (450°F+), more preferably 232-649°C (450-1200°F) (minor amounts, e.g., less than 10% of 649°C+ (1200°F+) material may be present). Preferably, the feed contains at least 90 wt% n-paraffins and boils in the range above 221°C (430°F).

[0020] The feed is preferably low in unsaturates, that is, low in both aromatics and olefins. Preferably, the unsaturates level is less than 10 wt%, preferably less than 5 wt%, more preferably less than 2 wt%. Also, the feed is relatively low in nitrogen and sulfur, e.g., less than 200 ppm of each, preferably, less than 100 ppm of each, more preferably less than 50 wppm of each. Where a Fischer-Tropsch derived feed is employed, there is no need to pre-sulfide the catalyst, and indeed, pre-sulfiding should be avoided.

[0021] Most preferably, the feed is the product of a Fischer-Tropsch reaction that produces essentially n-paraffins, and still more preferably the Fischer-Tropsch process is conducted with a non-shifting catalyst, e.g., cobalt or ruthenium, preferably a cobalt containing catalyst. The advantages of using a Fischer-Tropsch product as a feedstock reside in the high n-paraffin content and low heteroatom content of this feed.

[0022] The catalyst employed in the catalytic dewaxing step comprises a molecular sieve with one dimensional pore structure and a metal dehydrogenation component having an average diameter of 0.50 nm to 0.65 nm, and,

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preferably, the difference between the maximum diameter and the minimum diameter is ≤ 0.05 nm. This includes molecular sieves such as ZSM-23, ZSM-35, ZSM-22, SSZ-32, zeolite beta, mordenite and rare earth ion exchanged ferrierite. Preferably, a ZSM-48 catalyst is used containing a metal dehydrogenation functionality, preferably supplied by the presence of platinum or palladium or both platinum and palladium, preferably platinum. Other zeolites structurally equivalent to ZSM 48, such as EU-2, EU-11 and ZBM-30 may also be employed. ZSM-48 is particularly preferred. The use of catalysts based on these molecular sieves makes it possible to obtain low pour point lubricants in high yield at low pressure (less than 3549 kPa, 500 psig), and the process is characterized by low catalyst deactivation rates of less than 16.7 K (30°F)/ year.

[0023] The molecular sieves are well known in the art. They are for example described in J. Schlenker, et al., Zeolites 1985, vol. 5, November, 355-358.

[0024] ZSM-48 is characterized by the X-ray diffraction pattern shown in Table 1 below. The material is further characterized by the fact that it exhibits a single line within the range of 11.8 ± 0.2 Angstrom units. The presence of a single line at the indicated spacing structurally distinguishes ZSM-48 from closely related materials such as ZSM-12 (described in U.S. Patent No. 3,832,449) which has two lines, i.e., a doublet, at 11.8 ± 0.2 Angstrom units, and high silica ZSM-12 (described in U.S. Patent No. 4,104,294) which also has a doublet at the indicated spacing.

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Table 1

Characteristic lines of ZSM-48 (calcined, Na Exchanged Form)

d(A)	Relative Intensity (I/I ₀)
11.8±0.2	S
10.2±0.2	W-M
7.2±0.15	W
4.2±0.08	VS
3.9±0.08	VS
3.6±0.06	W
3.1±0.05	W
2.85±0.05	W

[0025] The values were determined by a standard technique, i.e., radiation was K-alpha doublet of copper, and diffractometer equipped with a scintillation counter. The peak heights, I, and the positions as a function of two times theta, where theta is the Bragg angle, were determined by a compactor. From these the relative intensities, 100 I/I₀, where I₀ is the intensity of the strongest line or peak, and d(obs.), the interplanar spacing in A corresponding to the recorded lines, were calculated. Table 1 gives the intensities in terms of the symbols W=weak, S=strong, VS=very strong, M=medium, and W-M=weak to medium (depending on the cationic form). Ion exchange of the sodium ion with other cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample, as well as any subsequent thermal treatment.

[0026] ZSM-48 and methods for its preparation are described in U.S. Patent Nos. 4,375,573; 4,397,827; 4,448,675; 4,423,021; and 5,075,269. The method

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of preparation described in U.S. Patent No. 5,075,269 is particularly preferred. This method is for preparing a catalyst particularly suitable for the catalytic dewaxing process.

[0027] The dehydrogenation component is preferably a noble metal, most often palladium or platinum, or both platinum and palladium. Platinum is the most preferred. The dehydrogenation component is most often present in an amount of 0.01 to 5.0 wt%, preferably 0.1 to 1.5 wt%, based on the catalyst total weight. Such component can be exchanged into the catalyst or the molecular sieve, impregnated thereon, or physically intimately admixed therewith. Such component can be impregnated in or onto the molecular sieve, such as, by treating the molecular sieve with metal-containing ion. In the case of platinum, suitable platinum compounds include chloroplatinic acid, platinous chloride and various compounds containing the platinum tetra-ammonia complex.

[0028] The compounds of the metals used to prepare the catalyst according to the present invention can be divided into compounds in which the metal is present in the cation of the compound and compounds in which it is present in the anion of the compound. Both types of compounds which contain the metal in the ionic state can be used. In the case of platinum, a solution in which platinum metals are in the form of a cation or cationic complex, e.g., $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, is particularly useful.

[0029] Prior to its use, the catalyst is usually at least partially dehydrated. This dehydration step is typically conducted to remove water from the catalyst. Excess water may cause steaming of the support material, leaching or migration of the metals, contamination of the products or other undesirable reactions. Dehydration can be done by heating to a temperature in the range of from 100°C to 600°C in an inert atmosphere, such as air, nitrogen, etc., and at atmospheric or

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subatmospheric pressures for between 1 and 48 hours. Dehydration can also be performed at lower temperature merely by placing the catalyst in a vacuum. The molecular sieve catalyst is formed in a wide variety of particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as extrudate having a particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst or the molecular sieve is molded, such as by extrusion, it can be extruded before drying or dried or partially dried and then extruded.

[0030] It may further be desired to incorporate the molecular sieve with a matrix material which is resistant to the temperatures and other conditions employed in the dewaxing process herein. Such matrix materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides e.g., alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates, sols or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the molecular sieve, i.e., combined therewith, which is active, may enhance the conversion and/or selectivity of the catalyst herein. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. Frequently, molecular sieves have been incorporated into naturally occurring clays, e.g., bentonite and kaolin. These materials function, in part, as binders for the catalyst. It is desirable to provide a catalyst having good crush strength since in a petroleum refinery the catalyst is often subject to rough handling which tends to break the catalyst down into powder-like materials which cause problems in processing.

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[0031] Naturally occurring clays which can be composited with molecular sieve include the montmorillonite and kaolin families which include the sub-bentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays, or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

[0032] In addition to the foregoing matrix materials, the molecular sieve can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel. Mixtures of these components can also be used. The relative proportions of the finely divided molecular sieve and the matrix material may vary widely. Generally the molecular sieve content ranges from 1 to 90 percent by total weight of the catalyst, and more usually from 2 to 80 percent.

[0033] One of the preferred catalysts according to the present invention is an alumina bound ZSM-48 molecular sieve, preferably containing 10-90 wt% zeolite crystals and up to 2 wt% platinum. These preferred catalysts have the advantages of exhibiting very low deactivation after prolonged use in dewaxing Fischer Tropsch derived wax.

[0034] In general, reaction conditions for dewaxing may vary widely even when the hydrogen partial pressures are maintained at low levels. Thus, start of run temperatures may vary between 288-343°C (550-650°F). End of run conditions can be defined by the nature of the product being produced, for example, when predetermined color specifications can no longer be met (an

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indication of catalyst deactivation), or when the predetermined pour point or cloud point can no longer be obtained, or the selectivity to isomerization is reduced as evidenced by an increase in methane yield due to hydrocracking. In general, however, end of run temperatures should be less than 427°C (800°F), preferably less than 399°C (750°F), more preferably less than 385°C (725°F). Reaction temperatures may for instance range from 288°C (550°F) to about 427°C (800°F). Reaction temperatures ranging from 288 to 385°C provide particularly good results.

[0035] According to a preferred embodiment of the present invention, hydrogen partial pressure is maintained as low as reasonably possible without sacrificing desired catalyst life. Catalyst life may be longer or shorter depending on desired results and severity of the dewaxing process, i.e., higher severity obtained by increasing temperature or decreasing feed velocity, or both. However, at end of run conditions the catalyst must be either rejuvenated or replaced, if rejuvenation is no longer possible. In either case the unit must be shut down and valuable operating time is lost. Because the process of the invention gives lower catalyst deactivation rates, the unit can be kept on-stream for an extended period of time.

[0036] In the process of the present invention, the catalyst deactivation rate is preferably less than 13.9 K (25°F)/year, more preferably less than 11.1 K (20°F)/year, and still more preferably less than 5.6 K (10°F)/year. Such catalyst deactivation rate at dewaxing conditions most often allows the process of the present invention to be carried out, while still meeting a predetermined pour point of less than -12°C, for a period of at least six months, preferably at least twelve months, more preferably at least 18 months, and still more preferably for at least 24 months, or longer, for example, greater than 30 months or greater than 36 months without catalyst replacement.

[0037] With the preferred process according to the invention, the catalyst's temperature increase required for meeting a pre-determined pour point of -21°C is less than 16.7°C (30°F)/year, more preferably less than 14°C (25°F)/year, still more preferably less than 11°C (20°F)/year, and still more preferably less than 5.6°C (10°F)/year.

[0038] Catalyst deactivation is believed to be a result of coke formation on the surface of the catalyst, the coke covering or blocking access to the catalytic metal, as well as blocking the pores of the zeolite. The catalyst may be regenerated by known methods including hot hydrogen stripping, coke removal by oxygen treatment or a combination of hydrogen stripping and oxygen treatment. Briefly, hydrogen stripping can be carried out with hydrogen or a mixture of hydrogen and an inert gas such as nitrogen, at isomerization reaction temperatures for a period of time sufficient to allow the catalyst to regain at least about 80%, preferably at least about 90% of its original lined out activity. Oxygen treatment can be carried out at calcining conditions, e.g., using air at temperatures from 500°C to 650°C , again for a period of time sufficient to allow the catalyst to regain at least 80%, preferably at least 90% of initial lined out activity after subsequent reduction.

[0039] The catalyst life requirements can be satisfied with hydrogen partial pressures of less than 3549 kPa (500 psig), preferably less than 2859 kPa (400 psig), more preferably positive hydrogen partial pressures greater than 101.325 kPa (0 psig) and less than 2859 kPa (400 psig), most preferably at hydrogen partial pressures ranging from 791 - 2859 kPa (100-400 psig), such as 791 - 2515 kPa (100-350 psig), and still more preferably at about 1136 - 2515 kPa (150-350 psig).

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[0040] In the process of the invention, the feed is contacted under hydrodewaxing conditions including a hydrogen partial pressure of less than about 3549 kPa (500 psig) with the catalyst, and the process temperature is adjusted (increased) whenever a pre-determined pour or cloud point is not met. A pour point of less than -12°C is preferred, and a pour point of about -18°C or less is more preferred.

[0041] At a hydrogen partial pressure of less than 3549 kPa (500 psig) and a pour point of -12°C or less, a typical deactivation rate is less than 16.7K (30°F)/year. Preferably at a hydrogen partial pressure of less than 3549 kPa (500 psig) and a pour point of about -18°C or less, a typical deactivation rate is less than 16.7 K (30°F)/year. In a most preferred embodiment, at 1136 - 2515 kPa (150-350 psig) hydrogen partial pressure and a pour point of about -21°C or less, a typical deactivation rate is less than 8.3 K (15°F)/year.

[0042] In general, other gases may be present that will not interfere with the reaction. Such other gases may be nitrogen, methane, or other light hydrocarbons (that may be produced during the reaction). Total pressure may range up to 13790 kPa (2000 psi), preferably 690 -13790 kPa (100-2000 psi), more preferably 1034 - 6895 kPa (150-1000 psi), still more preferably 1034 - 3447 kPa (150-500 psi). Hydrogen can make up 50-100% by volume of total gas, preferably 70-100% by volume, more preferably 70-90% by volume. At the low hydrogen partial pressures recited herein, small amounts of olefins and aromatics may be produced, and hydrofinishing, at well known conditions, may be necessary to remove these components.

[0043] The liquid hourly space velocity is generally between about 0.1 and about 10 volume of feed per volume of catalyst per hour, and preferably is generally between about 0.5 and 4. The hydrogen to feed ratio is generally

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between about 17.8 and about 1781, and preferably between about 142.5 and about 712.5 liter of hydrogen per liter of feed at standard conditions of 101.325 kPa and 15.5°C.

[0044] Alpha Value is an indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and provides a relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). The value is based on the activity of a silica-alumina cracking catalyst taken as an Alpha of 1 (rate constant = 0.016 sec^{-1}). The test for Alpha Value is described in U.S. Patent No. 3,354,078 and in the Journal of Catalysis. vol. 4, p. 527 (1965); vol. 6, p. 278 (1966); and vol. 61, 395 (1980). The Alpha Value of the catalyst used in the present invention prior to metal loading is preferably in the range of about 10 to about 50.

[0045] According to a particular embodiment the product of the dewaxing reaction is further subjected to a hydrotreating reaction. Such reaction consist of contacting the catalyst with a hydrofinishing catalyst, containing an active metal component sufficient to saturate a desired portion of olefins and aromatics which may be present, as is well known in the art.

[0046] The products obtained with the process according to the present invention exhibit particularly good properties. Also, the process according to the invention allows for the production of a low pour point lube product with a remarkable low yield of low value cracked fuel products while still showing good activity maintenance.

[0047] The following examples serve to illustrate this invention:

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EXAMPLE 1

[0048] This example shows the benefits in lube base oil yield obtained as hydrogen partial pressure is reduced from 3549 - 1136 kPa (500 to 150 psig). The following unit conditions and process variables were studied with ZSM-48 using a wide cut Fischer-Tropsch feed, i.e., 221°C+ (430°F+) feed.

[0049] Catalytic dewaxing was carried out in a downflow reactor simulating a trickle bed reactor immersed in a sand bath to maintain isothermal reactor conditions. The reactor contained 80 cc of an unsulfided ZSM-48 catalyst containing 35% alumina matrix with 0.6 wt% Pt based on total weight diluted with glass beads. Conversion of a 221°C+ (430°F+) wax obtained from a cobalt slurry catalyzed Fischer-Tropsch process was controlled by temperature.

[0050] The process was operated at temperatures ranging from 304-338°C (580-640°F) with reactor hydrogen pressures, at the reactor exit of 1136-3549 kPa (150-500 psig). The hydrogen treat gas rate was 320.6-445 liter of hydrogen per liter of feed at standard conditions of 101.325 kPa and 15.5°C, and the liquid hourly space velocity was 1.25v/v/hr.

[0051] The liquid product was fractionated by 15/5 distillation unit and the following fractions were recovered: IBP/160°C (320°F), 160°C/371°C (320/700°F), and 371°C+ (700°F+). The 371°C+ (700°F+) fraction was analyzed for pour and cloud points, and kinematic viscosity and viscosity index; the 160°C/371°C (320/700°F) fraction was analyzed for cloud point.

[0052] In Figure 1, lines A, B, and C refer to hydrogen pressures of 1136, 1825 and 3549 kPa (150, 250 and 500 psig). At a pre-determined pour point of

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-21°C, catalytic activity increases with decreasing operating pressure, as shown in Table 2 below.

Table 2

<u>Operating H₂ Pressure, psig/kPa</u>	<u>Temperature required for -21°C P.P.</u>
500/3549 (comparative)	627.4
250/1825	612.8
150/1136	602.8

[0053] The invention is based, inter alia, on the finding that the kinetics of the dewaxing process described herein is negative second order in hydrogen, so that the yield will increase with a reduction in hydrogen partial pressure, but, surprisingly and contrary to common belief, by using specific conditions and catalysts, the catalyst deactivation rate was kept remarkably low.

[0054] Selectivity to lubes increased with decreasing hydrogen pressure. In Figure 2, where lines A, B, and C again refer to hydrogen pressures of 1136, 1825 and 3549 kPa (150, 250 and 500 psig). The lubes yield, (i.e., 1-conversion), at a -21°C pour point is shown for each pressure in Table 3, below.

Table 3

<u>Operating H₂ Pressure, kPa/psig</u>	<u>Lubes Yield, at -21°C P.P., %</u>
3549/500 (comparative)	66.7
1825/250	73.9
1136/150	77.7

[0055] The data surprisingly show that catalyst activity and lube selectivity increased at lower pressure. Consequently, overall lube yield increased.

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[0056] Nevertheless, the prevailing wisdom is that catalyst life decreases substantially as hydrogen pressure decreases, thereby leading to shortened on stream periods and longer down times. To determine the effect of reduced hydrogen pressure on catalyst life (and the rate of catalyst deactivation) another experiment was conducted over a period of 70 days at 1136 kPa (150 psig) hydrogen pressure and producing lube base oil of -21°C pour point. By regression, the deactivation rate was 11.7K (21°F)/year, by two point activity check the deactivation rate was 14.4 K (26°F)/year.

[0057] Consequently, operating at a very low hydrogen pressure results in a good deactivation rate, and clearly shows that hydrogen pressures of less than 3549 kPa (500 psig), preferably less than 2859 kPa (400 psig), more preferably less than 1136 kPa (150 psig), e.g., 963 kPa (125 psig), or less than 791 kPa (100 psig), e.g., about 619 kPa (75 psig), will benefit both selectivity to isomerization and increased lube base oil yield while maintaining deactivation rates of less than about 16.7 K (30°F)/year, or preferably less than about 13.9 K (25°F)/year, and more preferably less than about 8.3 K (15°F)/year.

EXAMPLE 2

[0058] The reactor described in Example 1 was operated with a 221°C+ (430°F+) wide cut Fischer-Tropsch wax feed to study the operation of a dewaxing unit at 1825 kPa (250 psig). The catalyst of Example 1 was used, as well. The hydrogen treat gas rate was 445.3 liter of hydrogen per liter of feed (2500 SCF/bbl) at standard conditions of 101.325 kPa and 15.5°C. The liquid hourly space velocity was 1.0. Temperature was adjusted to meet lube pour point or diesel cloud point. When operated to meet a diesel cloud point of -15°C, the deactivation rate was less than 1 K/year (1.8°F/year). The results are shown in Figure 4.

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[0059] Operation of this unit to meet a -21°C wide-cut lube pour point resulted in a deactivation rate of about 3 K/year (5.4°F/year). The results are shown in Figure 5.

EXAMPLE 3

[0060] The same feed as used in Example 1 was hydroisomerized and the isomerate was distilled into two fractions: (i) 371°C-510°C (700-950°F) light cut, and (ii) a 510°C+ (950°F+) heavy cut. Each fraction was processed in the reactor described in Example 1 and conditions described in Example 2 to meet a -21°C pour point and a cloud point of +8°C, respectively. Each fraction was run for four (4) months. The results are shown in Figures 6 and 7; Figure 6 showing a deactivation rate (by regression) for fraction (i) of about 1.1 K (2°F)/year, Figure 7 showing a deactivation rate (by regression) for fraction (ii) of about 1.1 K (2°F)/year.

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CLAIMS:

1. A catalytic dewaxing process comprising contacting a feed containing at least 80 wt% of n-paraffins at dewaxing conditions including a hydrogen partial pressure of less than 3549 kPa (500 psig) with a catalyst comprising a molecular sieve with a one dimensional pore structure having an average diameter of 0.50 to 0.65 nm and a metal dehydrogenation component, the catalyst having a deactivation rate, measured by temperature increase required (TIR) for meeting a pre-determined pour point or cloud point, of less than about 16.6 K/year (30°F/year).
2. The process of claim 1 wherein the hydrogen partial pressure is greater than 101.325 kPa (0 psig).
3. The process of claim 1 or claim 2 wherein the hydrogen partial pressure is less than 2859 kPa (400 psig).
4. The process of any of the preceding claims wherein the hydrogen partial pressure is between 1136 kPa-2514.5 kPa (150 - 350 psig).
5. The process of any one of the preceding claims wherein TIR is less than 13.9 K/year (25°F/year).
6. The process of any one of the preceding claims wherein the paraffin containing feed contains greater than 90 wt% n-paraffins and boils in the range above 430°F.

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7. The process of any one of the preceding claims wherein the feed is derived from a Fischer-Tropsch process and contains less than 50 wppm each of nitrogen and sulfur.

8. The process of any of the preceding claims wherein the dehydrogenation component comprises platinum, palladium or mixtures thereof.

9. The process of any one of the preceding claims wherein the molecular sieve is selected from ZSM-23, ZSM-35, ZSM-48, ZSM-22, SSZ-32, zeolite beta, mordenite, rare earth ion exchanged ferrierite and mixtures thereof.

10. The process of claim 9 wherein the catalyst is an alumina bound ZSM-48 catalyst containing 10-90 wt% ZSM-48 and up to 2 wt% palatinum.

11. The process of any one of the preceding claims wherein the reaction temperatures range from 288°C to 427°C (550°F to 800°F).

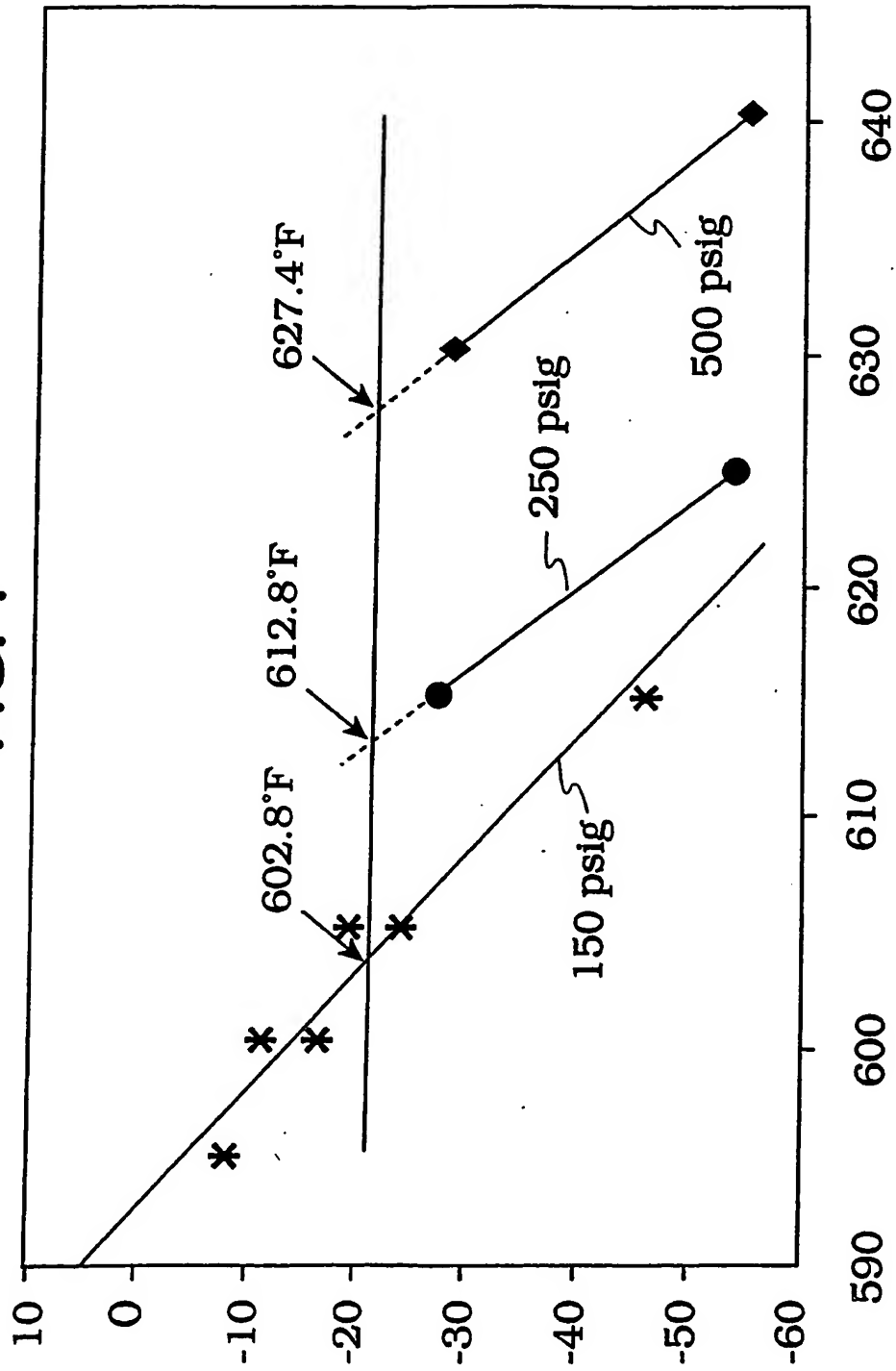
12. The process of any one of the preceding claims wherein the total reaction pressure ranges from 689 to 13790 kPa (100 to 2000 psi).

13. The process of any one of the preceding claims wherein the dewaxed product is further subjected to hydrofinishing.

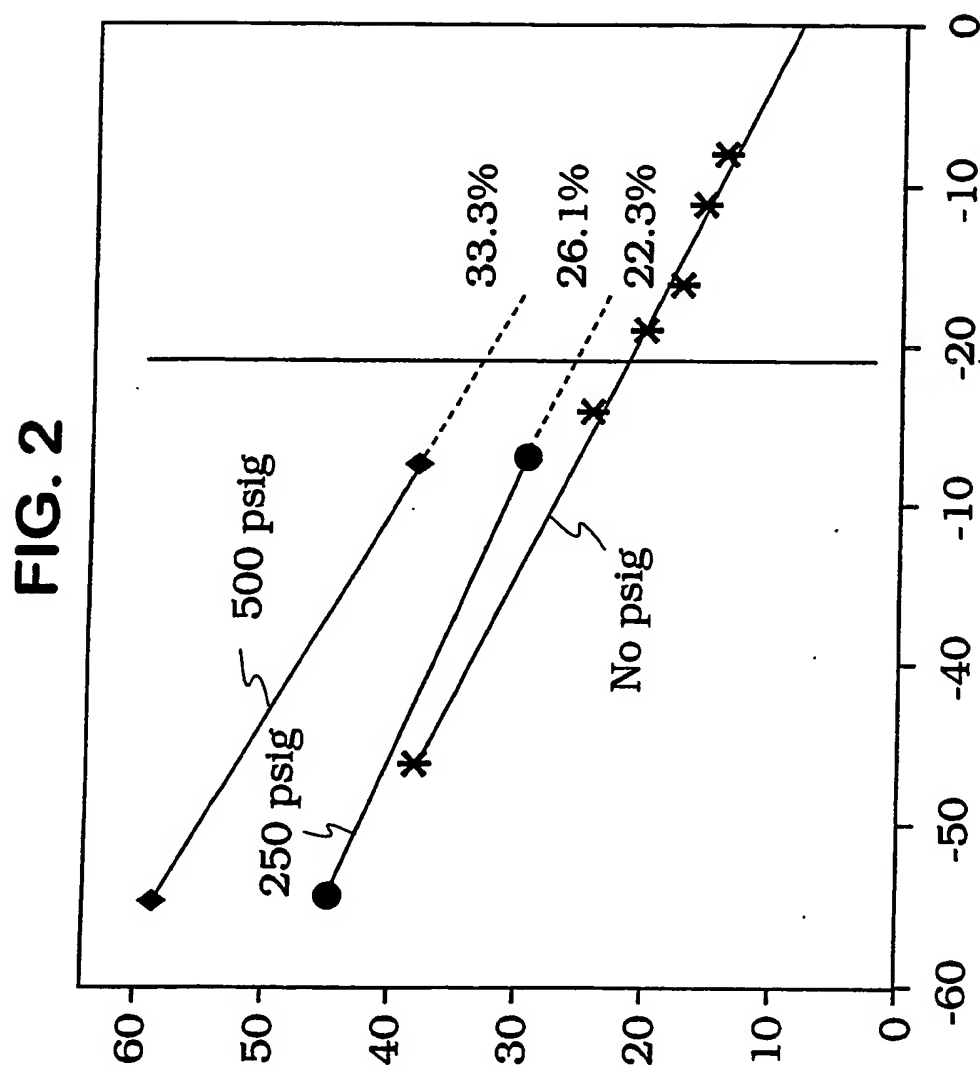
14. Use of the process according to any one of the preceding claims for the production of lube base stock or a diesel material.

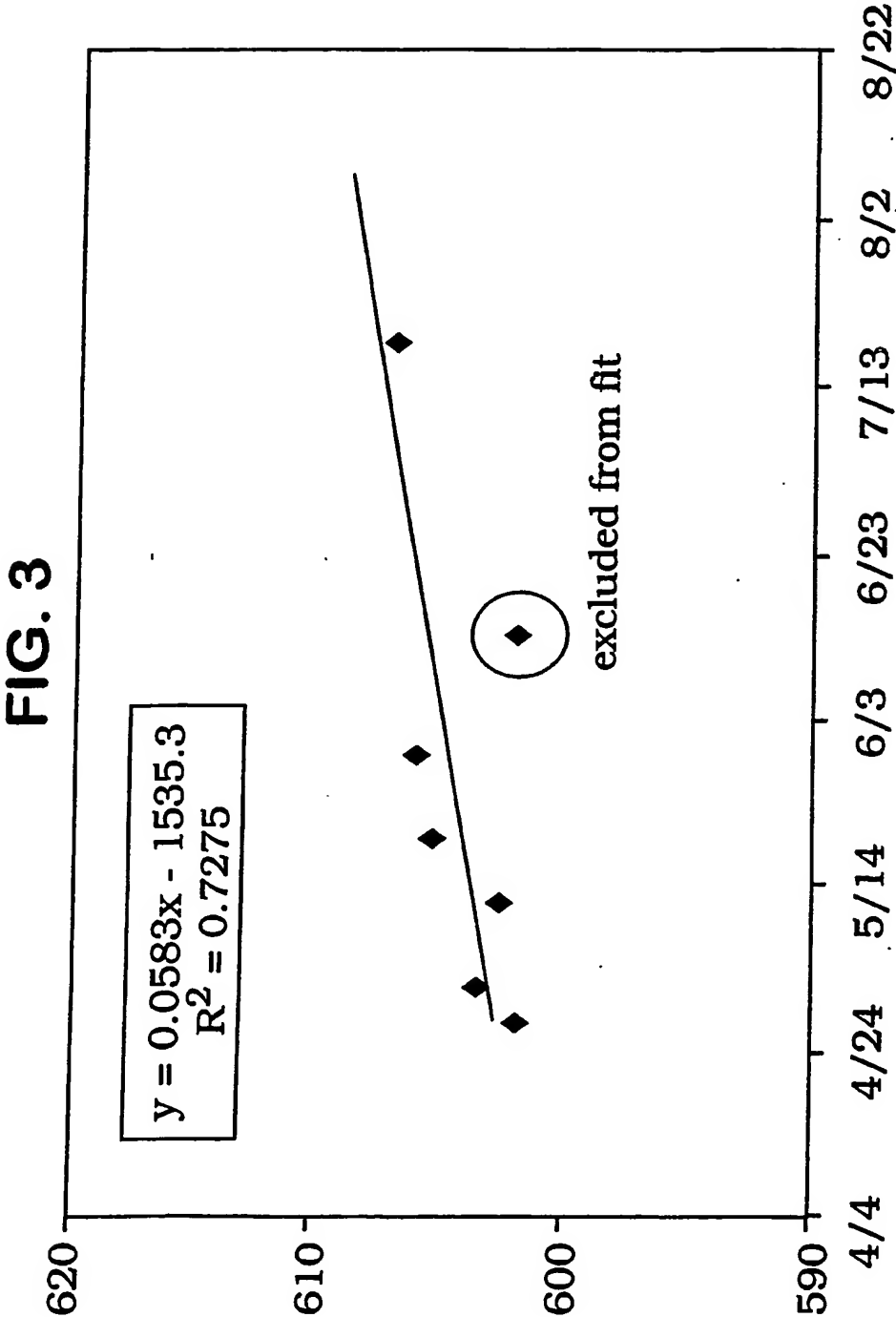
15. Use of the process according to any one of the claims 1 to 13 for improving the pour point or cloud point of a Fischer Tropsch product.

FIG. 1



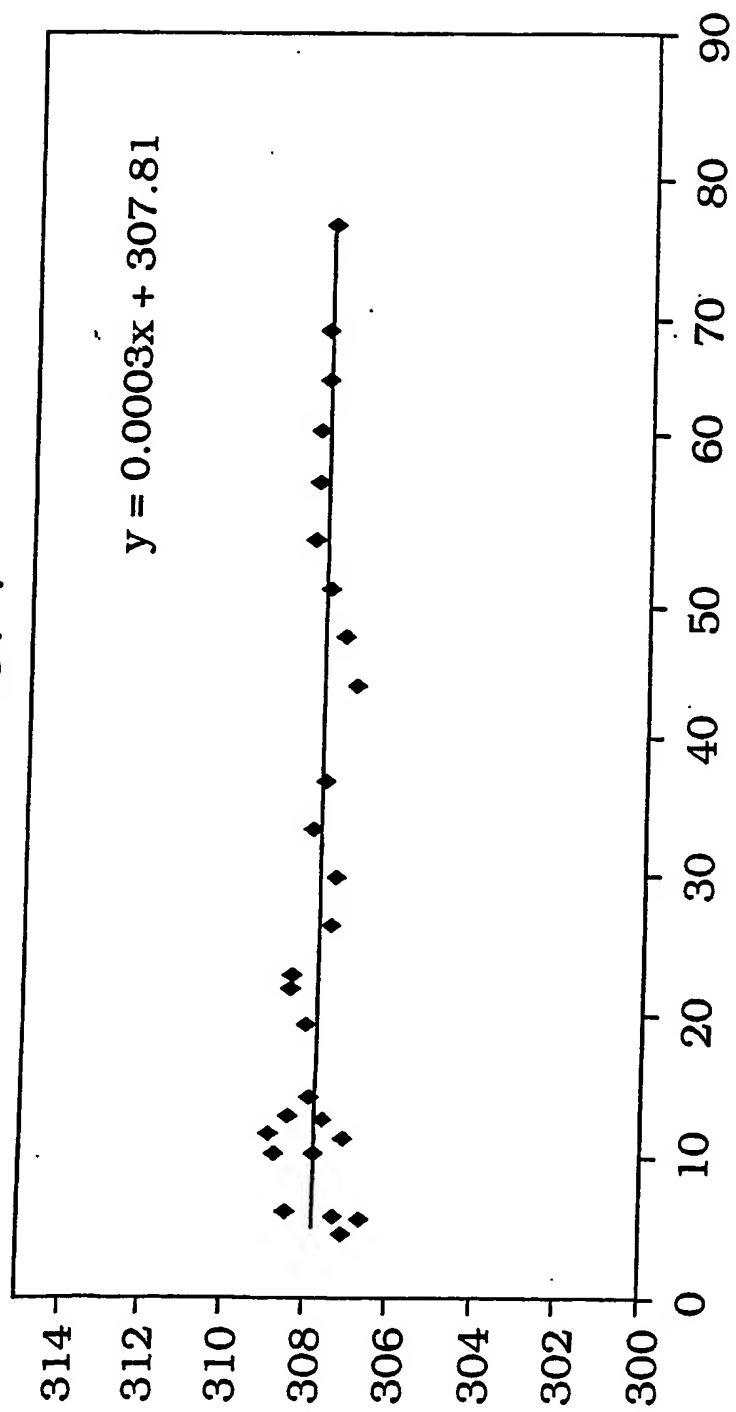
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FIG. 4



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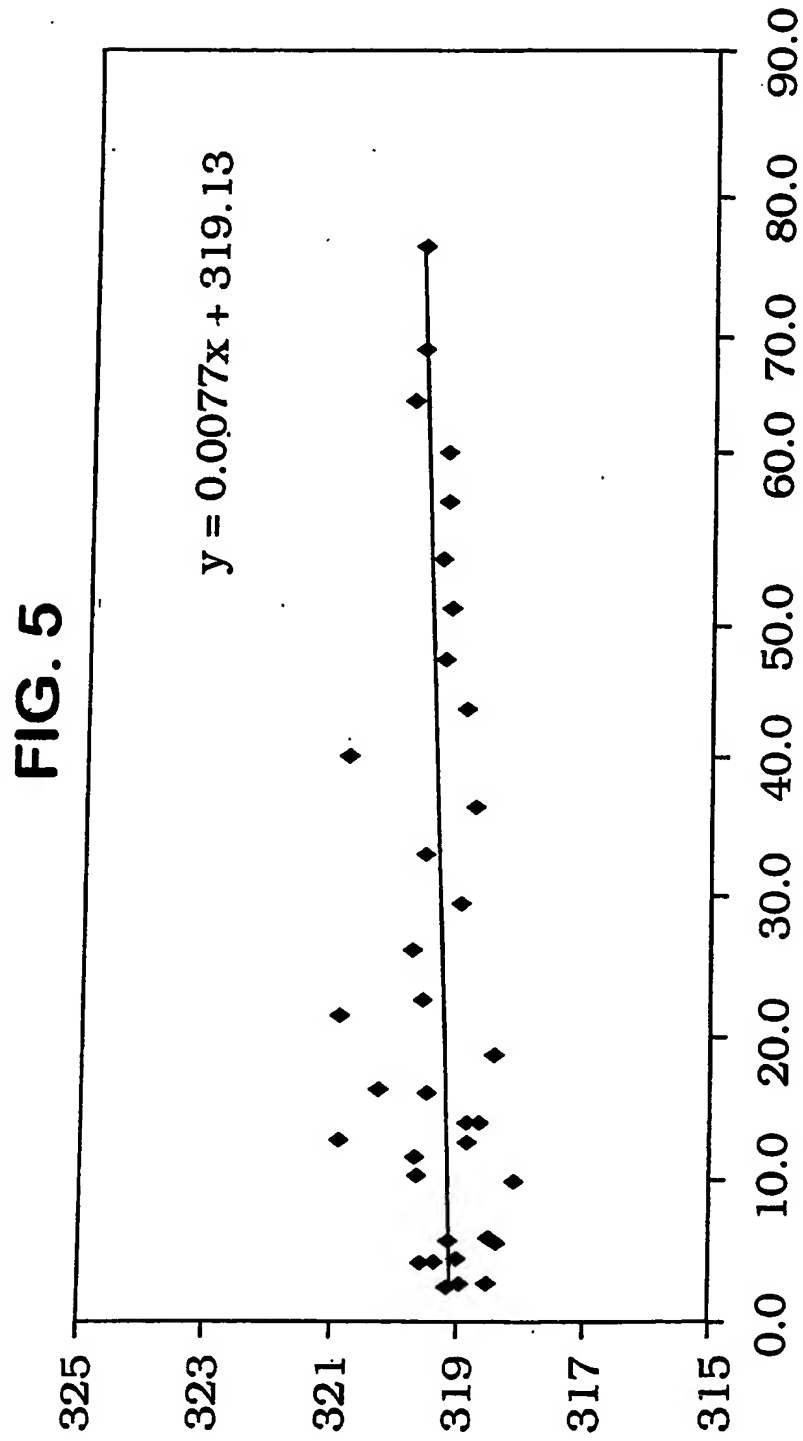
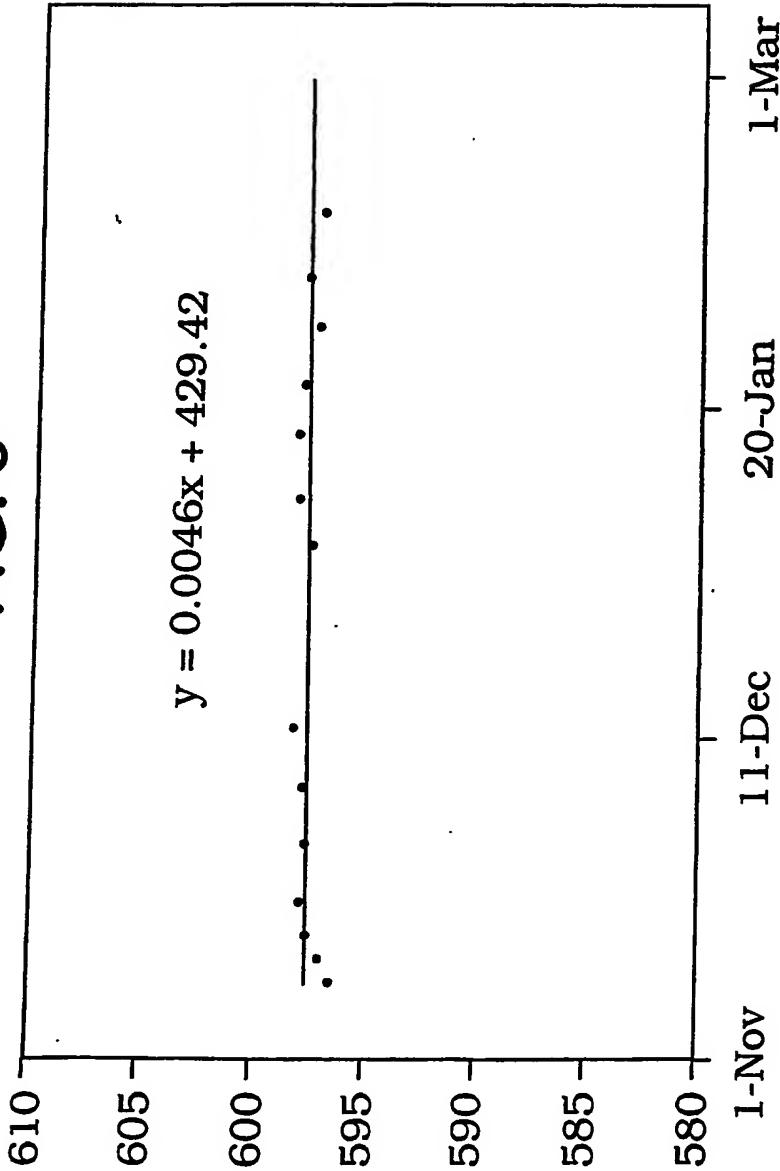
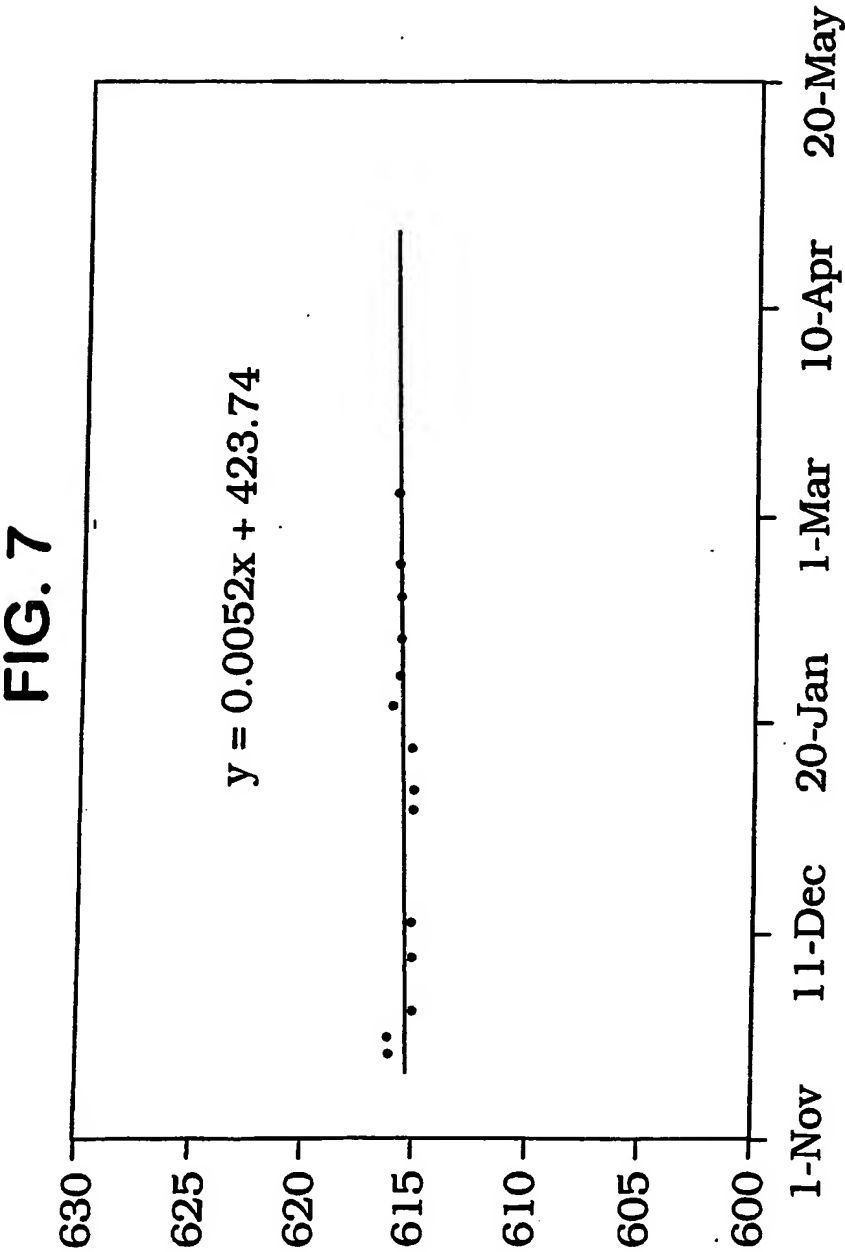


FIG. 6





A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G45/64 C10G65/04 C10G65/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 362 378 A (SCHRAMM SUZANNE E ET AL) 8 November 1994 (1994-11-08) cited in the application claims 1,10-12,14,19,22,24; example 1 column 2, line 25-30,52-57 column 5, line 26-30 column 7, line 24-28,46-62	1-15
X	US 4 872 968 A (BOWES EMMERSON) 10 October 1989 (1989-10-10) cited in the application claim 1; example 1 column 3, line 57 -column 4, line 4 column 5, line 4-9,28-30 column 9, line 20-28 column 9, line 51 -column 10, line 2 column 12, line 43-48	1-15



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

3 March 2004

Date of mailing of the international search report

10/03/2004

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Harf, J

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 03359 A (MOBIL OIL CORP) 8 February 1996 (1996-02-08) claims 1,3,4; example 1; table 1 page 5, line 8-16 page 6, line 26-29 page 7, line 11-15 page 9, line 28 -page 10, line 10 page 11, line 13-21	1-15
X	US 5 614 079 A (MCWILLIAMS JOHN P ET AL) 25 March 1997 (1997-03-25) claim 1 column 6, line 17-22,61-67 column 7, line 18-37 column 8, line 11-33	1-15
X	US 4 975 177 A (GARWOOD WILLIAM E ET AL) 4 December 1990 (1990-12-04) claims 1,11 column 5, line 24-33,44-54 column 6, line 33-51 column 9, line 4-37 column 11, line 6-12,28-33	1-15
A	US 4 599 162 A (YEN JEFFREY H) 8 July 1986 (1986-07-08) claims 1,2 column 4, line 4-35,45-50 column 5, line 7-9 column 7, line 49-64 column 8, line 63-66	1-15
A	US 4 808 296 A (CHEN NAI Y ET AL) 28 February 1989 (1989-02-28) claim 1 column 2, line 27-40 column 3, line 20-23 column 4, line 4,5,38-50 column 4, line 67 -column 5, line 21	1-15

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5362378	A	08-11-1994	WO 9603359 A1 AU 7474494 A SG 66235 A1 AU 695832 B2 DE 69421100 D1 DE 69421100 T2 EP 0783470 A1	08-02-1996 22-02-1996 20-07-1999 20-08-1998 11-11-1999 20-01-2000 16-07-1997
US 4872968	A	10-10-1989	AT 72674 T AU 611183 B2 AU 2003088 A CA 1302935 C CN 1040613 A ,B DE 3868458 D1 EP 0304252 A1 ES 2029519 T3 IN 171953 A1 JP 1144492 A JP 2609466 B2 KR 9607734 B1 ZA 8806181 A	15-03-1992 06-06-1991 23-02-1989 09-06-1992 21-03-1990 26-03-1992 22-02-1989 16-08-1992 20-02-1993 06-06-1989 14-05-1997 11-06-1996 25-04-1990
WO 9603359	A	08-02-1996	US 5362378 A WO 9603359 A1 AU 695832 B2 AU 7474494 A DE 69421100 D1 DE 69421100 T2 EP 0783470 A1 SG 66235 A1	08-11-1994 08-02-1996 20-08-1998 22-02-1996 11-11-1999 20-01-2000 16-07-1997 20-07-1999
US 5614079	A	25-03-1997	US 5365003 A SG 96157 A1 WO 9603360 A1 US 5541146 A	15-11-1994 23-05-2003 08-02-1996 30-07-1996
US 4975177	A	04-12-1990	US 5037528 A AT 78048 T AU 603344 B2 AU 6399086 A BR 8605401 A CA 1307487 C CN 86107556 A DE 3685943 D1 DE 3685943 T2 EP 0225053 A1 JP 1944921 C JP 6062960 B JP 62112691 A KR 9311924 B1 US 4919788 A US 4911821 A	06-08-1991 15-07-1992 15-11-1990 07-05-1987 11-08-1987 15-09-1992 07-10-1987 13-08-1992 04-03-1993 10-06-1987 23-06-1995 17-08-1994 23-05-1987 22-12-1993 24-04-1990 27-03-1990
US 4599162	A	08-07-1986	NONE	
US 4808296	A	28-02-1989	NONE	